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IMPORTANCE AND SIGNIFICANCE OF TRANSITION TEMPERATURES  
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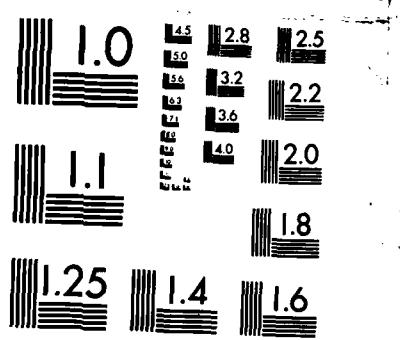
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by

W. A. Lee

November 1984

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**IMPORTANCE AND SIGNIFICANCE OF TRANSITION TEMPERATURES**

by

W. A. Lee

SUMMARY

The importance of the transition temperatures of polymers is described with particular emphasis on their practical significance. An outline of the RAE Transition Temperature Data Bank is provided and RAE publications in the transition temperature field are tabulated.



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## 1 INTRODUCTION

This Memorandum is one of a series of reports and memoranda relating to the transition temperature (TTs) of polymers and explains briefly the motivation for studies in this area. The important part played by TTs in determining the properties of polymers is described with many examples of their practical significances. A keen academic and commercial interest in TTs is illustrated by reference to the RAE Transition Temperature Data Bank; RAE publications in the TTs field are listed.

## 2 IMPORTANCE AND SIGNIFICANCE OF TRANSITION TEMPERATURES

Over the last decade, a large number of polymers have been synthesised yet only a small proportion has achieved commercial success. Leaving aside those polymers synthesised solely for academic reasons, the origins of this failure are at least twofold. Firstly, there are many commercial polymers already available and between them they provide a wide spectrum of useful properties which makes it increasingly difficult to bring about a significant improvement on a cost effective basis. Secondly, the designing of new polymers for specific properties, 'molecular engineering', has sometimes been more hit and miss than it might have been. Nevertheless, there are important gaps at the top and bottom of the temperature scale and for special applications, and it becomes increasingly compelling to make more effective use of the vast amount of data currently available and direct new research into more profitable channels. To this end, many investigations are concerned with the relationships between structure and properties in order to make the best possible estimate of properties in advance of synthesis. In pursuit of this aim, an understanding is required of the main factors which govern polymer properties. A totally crystalline polymer, if such could be obtained, would be very brittle and not very useful. It follows therefore, that the state of the amorphous (non-crystalline) regions is one of the dominant factors insofar as physical, particularly mechanical, properties are concerned which determine, the degree of usefulness of a material. Differences in the physical properties of linear polymers are determined by variations in the types and rates of segmental motion of the polymer chains and the types and degrees of molecular ordering. Changes in the characteristics of the amorphous or crystalline regions occur at the TTs and it follows therefore that they are all important in determining the properties of a polymer. For example, transitions associated with the amorphous region determine the low temperature limit of the high reversible strain characteristic of elastomers, the moulding and the upper and lower service temperatures and to some degree the toughness of plastics, and the drawing temperature of fibres. In general terms, all physical properties of amorphous polymers which depend on the segmental relaxation rate undergo a major change on heating through the glass transition temperature ( $T_g$ ) region. A plastic material which is largely amorphous may show a large drop in Young's modulus (perhaps 3 orders of magnitude) and, at the same time, a discontinuity in the temperature dependence of, or a marked change in, such properties as diffusivity, expansivity, refractive index, gas solubility, crazing, creep, damping, adhesion and chemical reactivity. For satisfactory strength and stiffness, many thermoplastic commercial polymers, particularly fibres, must have both the type and degree of

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crystallinity controlled within appropriate limits. At the temperatures of crystal-crystal transitions ( $T_{ccs}$ ), changes in density and mechanical properties can occur and at the melting point ( $T_m$ ) there is a catastrophic fall in strength and stiffness in crystalline polymers.  $T_m$ ,  $T_{ccs}$ , and crystallisation temperatures assume considerable importance in governing the temperatures of processing.

It is evident that before embarking on any programme of polymer development or synthesis, close attention must be given to both amorphous and crystalline region TTs. The amassing of reliable and comparable information on TTs is the first step in the attempt to resolve what sort of polymer will have the properties desired. It also yields much of the data needed to be able to decide whether an existing polymer has the required properties or may be further developed to do so.

In practical terms, the number of fields and applications in which a necessary interest in TTs has been shown is illustrated by the example index terms drawn from the RAE Transition Temperature Data Bank (see Appendix A) which was formed in co-operation with RAPRA and covers data up to 1979. Since that date, references to TTs have been recorded as a result of computer searches, but the references have mostly not been processed. An enormously diverse field of applications and interests is shown by the 1800 titles in the actual index. Appendix B briefly describes the RAE Data Bank the size of which is a measure of external interest in TTs and therefore of their significance to workers in the polymer field.

RAE papers and publications on transition temperatures have attracted much interest<sup>1-20</sup> as can be judged from over 100 citations in the Science Literature Index and correspondence on the subject from over 140 different persons.

### 3 CONCLUSIONS

Transition temperatures determine what sort of material (elastomer, plastic or fibre) a polymer may be, its temperature limitations, or advantages, in processing and in use, whether or not it will be in the glassy or rubbery state at its use temperature, and the temperatures at which some of the more significant changes in physical properties occur. They are of the greatest importance to the engineer as well as to the scientist trying to make new polymers with improved properties and to correlate properties with structure, indeed it has been said that "it is impossible to understand the properties of polymers without a knowledge of the types of transitions that occur in such materials. Nearly all the properties of polymers are determined primarily by these transitions and the temperatures at which they occur"<sup>21</sup>.

Appendix AEXAMPLES OF INDEX TERMS USED IN THE RAE TRANSITION TEMPERATURE DATA BANK

Abrasion	Damping /Vibration damping
Activation energy	Deformation
Adhesion, adhesive	Deformation energy
Adhesive sheet	Degradation
Adhesive tape	Densified vol.
Ageing see also/Degradation	Density
Aircraft window	Dental crowns
Allotropy	Depolarisation current
Annealing	Dielectric properties
Antioxidant	Dielectric relaxation
Antiplasticiser	Diffusion
Artificial leather	Dimensional stability
Bearings	Drape stiffness
Binding power index	Drawing, /Drawn
Biomedical	Drawing temperature
Birefringence	Dyeing
Bond interchange	Dynamic mechanical
Bottle	Elasticity
Brillouin scattering	Elasticity minimum temperature
Carbohydrate	Elastomers
Car interior	Electrets
Casting solvent	Electrical conductivity
CED see/Cohesive energy density	Electrical insulation
Chemiluminescence	Electrical resistance
Clathrate	Electric discharge
Coating compositions	Elongation
Cohesive energy density (CED)	Elongation ratio
Cold forming	Emulsion freeze-thaw stability
Cold rolling	Encapsulation
Compressibility	Energy of rotational isomerisation
Conduction/elect. Conductivity/elect.	Etching
Cracking	Excluded volume
Crease recovery	Expansion coefficient
Creep	Explosives
Critical surface tension	Fabrication
Crystallinity	Fabric production
Crystallisation	Failure envelopes see Ultimate properties
Crystallisation (Rate)	Fatigue
Crystallisation Temp	Fibres
Current regulating	6T Fibre

Fibrillation	Luminescence
Filler	Magnetic field
Films	Magnetic tape
Fire retardant	Mechanical behaviour
Flatspot index	Medical implant
Flex abrasion	Membrane
Flexibility	Minimum film fusion temperature
Flow temp.	Modulus
Fluids	Molar Ht.
Footwear	Molar volume
Fracture	Molec motion
Free volume	Mooney viscosity
Freezing point	Moulding
Friction	Natural leather
Gas chromatography	Necking
GEM disubstitution	Nucleation
Glass reinforced plastics	Oil
Golf balls	Optical activity
Grafting	Ozone cracking
Granulating	Packaging
Grease	Paint
Hardener see/Crosslinking (Structure)	Paper coating
Hardness	Peeling strength
Heat capacity	Penetrant
Heat conductivity	Permeation, /Permeability
Heat distortion	Phase equilibria
Hot pressing	Phosphorescence
Impact (Resilience) (Resistance) (Strength)	Photodegradation
Internal friction	Pipe couplings
Internal pressure	Plastic yield
Interpenetrating polymer network	Poisson's ratio
Interplanar slippage	Polishes
Ionic charge	Polymer characterisation
Irradiation	Polymer design
Ladder polymers	Polymer networks
Lamella thickness	Polymerisation conditions
Lamination	Powder preparation
Laser-induced damage	Processability
Latex manufacture	Product design
Leather coating	Propellants
Leather substitutes	Propellant binders
Liquids	Puhl Coef
Load	Radiation aww Irradiation
Lubricant	Radical concentration

Reactivity  
Reduced electrical resistivity  
Refractive index  
Relaxation time  
Rigidity  
Rolling  
Safety glass  
Scintillation intensity  
Sealant  
Seals  
Sheet formation  
Shrinkage  
Surface tension  
Surgical  
Swelling  
Tearing  
Tear Strength  
Temperature conductivity  
Tensile properties  
Theory  
Thermal conductivity  
Thermal expansion  
Thermal history  
Solubility  
Solubility parameter  
Solution properties  
Sound velocity  
Specific heat  
Specific retention Volume  
Specific Volume  
Spherulitic growth rate  
Strain  
Stress-optical coef.  
Stress relaxation  
Stretching  
Thermal stability  
Transport  
Tyres  
Varnish see/Paint  
Vibration dampers  
Viscoelasticity  
Void formation  
Volume expansion  
Vulcanisation

Appendix BTHE RAE DATA BANK ON TRANSITION TEMPERATURES

As part of a programme on polymer development at RAE a data bank on transition temperatures of polymers was compiled. The majority of data related to transitions of the non crystalline phase of undiluted linear homopolymers, but a wider field of interest had been indexed to a limited extent. The data bank comprised:

- (a) Index of 10700 data cards showing transition temperatures of individual polymers.
- (b) Author index comprising 11000 entries (based on first-named authors).
- (c) Subject index with 1800 subject headings and 14500 referenced information cards.
- (d) Computer based index of 1200 critically assessed glass transition temperatures of undiluted linear homopolymers in a chemical hierarchy and  $T_g$  value order together with a suite of over 100 computer programs to manipulate the data. Data up to 1972 was published in the second edition of the Polymer Handbook<sup>1</sup>.
- (e) Handbook of Data Sheets on 90 carbon-chain fluoropolymers<sup>2</sup>
- (f) Handbook of Data Sheets on 197 fluoropolymers containing main-chain nitrogen<sup>3</sup>.
- (g) A Handbook of Data Sheets on fluoropolymers containing main-chain oxygen<sup>4</sup>.

## REFERENCES

<u>No.</u>	<u>Author</u>	<u>Title, etc</u>
1	W.A. Lee R.A. Rutherford	Glass transition temperatures. In <u>Polymer Handbook</u> , edited by J Brandrup, second edition, Section III, pp 139-192 J Wiley and Sons, Inc, New York, (1975)
2	W.A. Lee R.A. Rutherford	RAPRA Data Handbook. Polymer transition temperature data sheets, carbon chain fluoropolymers, Vol I. RAPRA, Shawbury, (1973)
3	W.A. Lee R.A. Rutherford	RAPRA Data Handbook. Polymer transition temperature data sheets, fluoropolymers containing main-chain nitrogen, Vol II, Parts 1 and 2. RAPRA, Shawbury, (1974)
4	W.A. Lee R.A. Rutherford	RAPRA Data Handbook. Polymer transition temperature data sheets, fluoropolymers containing main-chain oxygen or sulphur, Vol II, Parts 1 and 2 RAPRA, Shawbury, (1976)
5	W.A. Lee	An analysis of factors governing the glass transition temperatures of polymers based on a review of available measurements. RAE Report No.CPM 8 (1964)
6	W.A. Lee	Glass transition temperature of homopolymers: a bibliography and assessment of available data. RAE Technical Report 65151 (1965) Also published as Chapter III of <u>Polymer Handbook</u> , edited by J. Brandrup and E.H. Immergut, Interscience, NY, (1966)
7	W.A. Lee J.H. Sewell	The influence of cohesive forces on the glass transition temperatures of polymers. RAE Technical Report 65112 (1965) Also published in <u>J. Applied Polymer Science</u> , 12(6), 1397 (1968)

REFERENCES (continued)

<u>No.</u>	<u>Author</u>	<u>Title, etc</u>
8	W.A. Lee G.J. Knight	The ratio of the glass transition temperature to the melting point in polymers. RAE Technical Report 66005 (1966) Also published in British Polymer J., <u>2</u> , 73 (1970)
9	G. Allen W.A. Lee	A critical survey of current views of the glass transition phenomena. RAE Technical Report 66090 (1966)
10	W.A. Lee D. O'Mahony	Calculation of the glass temperatures of polymers having alkyl side chains. RAE Technical Report 66292 (1966) Also published in J. Polymer Sci., Pt A-2, <u>8</u> , 555 (1970)
11	W.A. Lee G.J. Knight	The glass transition temperatures of polymers. In Polymer Handbook, first edition, Edited by J. Brandrup and E.H. Immergut, (Section III, pages 61-91), published by J. Wiley and Sons, Inc, New York, (1966)
12	W.A. Lee	Some aspects of the problem of designing new heat-resistant fluids and elastomers; structures containing phenyleneperfluoroalkylene units. RAE Technical Report 66409 (1966)
13	J.M. Barton W.A. Lee	Definition of structural groups in the calculation of glass temperatures of homopolymers. RAE Technical Report 67119 (1967)
14	J.M. Barton W.A. Lee D. O'Mahony	Correlation of the glass transition temperatures of polyacrylates, polymethacrylates and polychloroacrylates with their chemical structures. RAE Technical Report 67298 (1967)
15	J.M. Barton W.A. Lee	Contribution of the methylene group to the glass transition temperatures of polymers. Polymer, <u>9</u> , 603 (1968)
16	W.A. Lee	Proposal for the evaluation of potentially flexible and heat resistant units in polymers. RAE Technical Memorandum Mat 67 (1969)

REFERENCES (concluded)

<u>No.</u>	<u>Author</u>	<u>Title, etc</u>
17	W.A. Lee B. Stagg	The internal plasticisation of aromatic polyesters by alkyl side chains. RAE Technical Report 71223 (1971)
18	W.A. Lee Shirley A. Watts	Correlation of the glass transition temperatures of carbon-chain fluoropolymers with their chemical structures. RAE Technical Report 74060 (1974)
19	W.A. Lee	Correlation of the properties of fluoropolymers with chemical structure. RAE Technical Memorandum Mat 195 (1974) (Invited paper presented at the 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland, September 1974)
20	W.A. Lee Shirley A. Fowler	Correlation of the glass transition temperatures of heteroatom-chain fluoropolymers with their chemical structures. RAE Technical Report 75043 (1975) (Commercial-in Confidence)
21	D.W. van Krevelen	Properties of polymers. Correlations with chemical structure. Elsevier Scientific Publishing Company, Amsterdam, second edition, page 20 (1976)

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